DEFINING THE BASELINE OF THE REE STABLE ISOTOPE VARIATIONS IN SOLAR SYSTEM MATERIALS: EARTH. J.Y. Hu[1], F.L.H. Tissot[1,2], R. Yokochi[1,3], T.J. Ireland[1] and N. Dauphas[1], [1]Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, Chicago IL, [2]Department of the Earth, Atmospheric and Planetary Sciences, MIT, Cambridge, MA, [3]Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, IL.

Introduction: Mass-dependent fractionations (MDFs) of stable isotopes record critical information regarding the origin and evolution of planetary materials [1]. Studies of MDF of refractory lithophile elements (RLEs) can provide insights into condensation/evaporation and planetary accretion processes in the early solar system. For example, the lighter calcium isotope composition observed in carbonaceous meteorites compared to that of the bulk silicate Earth, enstatite and ordinary chondrites [2, 3] may be due to the contribution of refractory dust [4, 5], which has a light Ca isotope composition [6, 7]. In contrast, titanium, another RLE with a similar chemical behavior in the early solar system, was found to have uniform isotope compositions among different groups of meteorites including carbonaceous chondrites [8]. A potential explanation for the dichotomy of these two refractory elements could be connected to the higher 50% condensation temperature of Ti relative to Ca [9]. The isotopic results suggest that no Ti net loss took place from the CAI-forming region, while not all Ca condensed in the CAIs [7, 8]. Clearly, more proxies are needed to better understand the processes that occurred during the condensation of the solar nebula.

Particularly promising are the rare earth elements (REEs), a group of RLEs that cover a significant range in terms of volatility (50% condensation temperatures ranging from ~1659 to 1356 K [9]). The wide range of volatility and their relatively immobile chemical property makes REE isotopes ideal tracers to unravel the thermal and accretion processes in the earliest stages of the solar system.

To date, study on isotopes of REEs has mainly focused on radiogenic systems (e.g., $^{147}Sm/^{143}Nd$, $^{146}Sm/^{142}Nd$). As such, isotope data about REE MDFs are very limited, especially for heavy REEs (HREEs) [10, 11]. Thus, we have started analyzing the isotope compositions of Nd, Sm, Eu, Gd, Dy, Er and Yb in different geological reference materials, in order to get a first approximate bulk silicate Earth isotope composition for these systems. The geological reference materials comprise four basalts (BIR-1a, BHVO-2, BCR-2, W-2a), one andesite (AGV-2), one granite (G3), and one carbonatite (COQ-1).

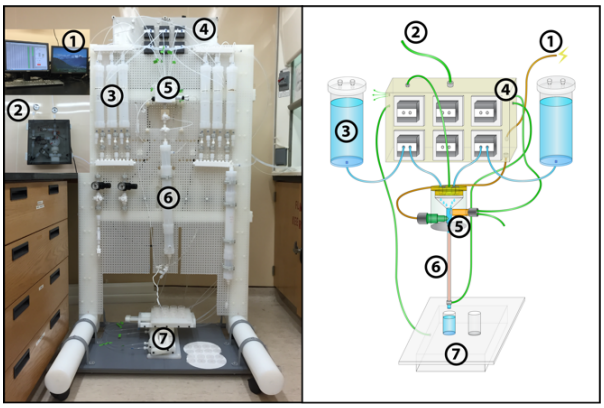

Figure 1: Schematic view of ChRobot. 1: computer control. 2: pneumatic actuation. 3: reagent reservoirs. 4. Positively pressurized electronic bay. 5: Mixing chamber. 6: Thermostatic column. 7: Moving stage for collection of elution cuts.

Methodology: As the REEs behave very similarly during column chemistry, a major problem for the accurate measurement of their mass-dependent isotope composition is the proper separation of the individual REEs from one another by ion exchange chromatography. To overcome this challenge, we developed an all-Teflon, pneumatically actuated high-performance liquid chromatography system, called ChRobot (short for Chromatography Robot; Fig. 1). The most distinctive features of ChRobot are: 1) The elution scheme is controlled by a computer via a LabView software interface, making it possible to achieve fine-step ramp elutions through the fresh mixing of as many as 6 reagents during an extensively long time period (e.g., 48h). Both features are impossible to achieve on traditional gravity-driven columns. 2) Almost all parts related to elution are made out of solid Teflon and are pneumatically actuated. Electronics are housed in a box that is positively pressurized and is spatially isolated from the liquid flow path. Compared to the first iteration of the instrument [12], this updated design reduces chances of contamination and ensures that ChRobot remains intact under the harsh clean lab environment that a commercial HPLC could not sustain. 3) The elution temperature is adjustable (up to 80 °C) thanks to a water circulation system, in order to achieve optimal separation. Mixed reagents are forced through the column via a pressurized chemically inert gas (N_2).

The pressure of N_2 is also adjustable (0 to 55 psi) to control the elution rate.

The use of ChRobot dramatically improves the efficiency of the chemical separations while maintaining a low blank and high reliability that is superior to traditional gravity-driven chromatography. The elution tests performed on the ChRobot show that all REEs isotope systems can be separated from each other with close to 100% yields and minor overlap (Fig. 2). The procedural blank during ChRobot elution is low, accounting for less than 30% of the overall blank; including digestion and preconcentration of the REEs (i.e., < 0.01 ng for Dy, < 0.005 ng for Er, and 0.05 ng for Yb).

All geostandards were doped with double spikes (Nd, Sm, Eu, Gd, Dy and Yb) before digestion. REEs are first extracted from the major elements using the TODGA resin, after which they are loaded into ChRobot for individual separation. Isolated REE solutions are evaporated to dryness and re-dissolved to concentrations between 10 to 20 ppb and measured for their isotope compositions using a Thermo Scientific MC-ICPMS upgraded to Neptune Plus specifications with the addition of an OnTool Booster pump. As there are no well-established isotope standards for REE isotopes, the isotope ratios of geostandards are normalized to our lab standards. These REE isotope standards are prepared from homogeneous, high purity oxide powder purchased from ESPI and are available upon request.

Results and Discussion: The typical external reproducibility of the isotopic measurements is approximately 0.02 per mil per amu for Nd, Sm, Gd, Dy, Er and Yb when using a double-spike, and 0.03 per mil per amu for Eu when using Dy external normalization. This is by about a factor of 4 smaller than the observed variation in the Ca isotope composition between different groups of chondrites [2, 3].

For most REEs, the isotope compositions of the geostandards that have been analyzed are found to be very homogeneous, which is consistent with the results reported in earlier study on europium and ytterbium isotopes for terrestrial samples [10]. Small variations are observed mainly between basaltic rocks and granites. This might be due to magmatic isotope fractionation. A first order estimated of the terrestrial composition relative to our lab isotope standards yields $\delta^{146/145}$Nd = -0.02 ‰, $\delta^{149/147}$Sm = +0.20 ‰, $\delta^{153/151}$Eu = +0.35 ‰, $\delta^{157/155}$Gd = +0.08 ‰, $\delta^{163/162}$Dy = -0.02 ‰, $\delta^{168/167}$Er = +0.07 ‰ and $\delta^{173/174}$Yb= -0.05 ‰.

Conclusions: We show that it is possible to measure the mass-dependent fractionation of Nd, Sm, Eu, Gd, Dy, Er and Yb to a precision of around 0.03 ‰/amu, which is expected to be sufficient to resolve MDF effects due to processes taking place during the condensation in the solar nebula. Isotope variations among different terrestrial geostandards is limited, which allows us to define a first estimate of the stable isotope compositions of REEs for the bulk silicate Earth.

References:

[1] Teng F et al. (2017) *Non-Traditional Stable Isotopes* ISBN 978-0-939950-98-0 [2] Simon J I and DePaolo D J (2010) *Earth Planet. Sci. Lett.* 289(3): 457-466. [3] Valdes M C et al. (2014) *Earth Planet. Sci. Lett.* 394: 135-145. [4] Dauphas N and Pourmand A (2015) *Geochim. Cosmochim. Acta.* 163: 234-261. [5] Barrat J A et al. (2016) *Geochim. Cosmochim. Acta.* 176: 1-17. [6] Huang S et al. (2012) *Geochim. Cosmochim. Acta.* 77: 252-265. [7] Simon et al. (2016) *LPSC* #1397. [8] Greber et al. (2016) *LPSC* #1448. [9] Lodders K (2003) *Astrophy. J.* 591(2): 1220. [10] Albalat E et al (2012) *Earth Planet. Sci. Lett.* 355: 39-50. [11] Albalat E et al. (2015) *Earth Planet. Sci. Lett.* 429: 147-156. [12] Ireland (2013) *Chemical Geology*. *357*, 203-214.

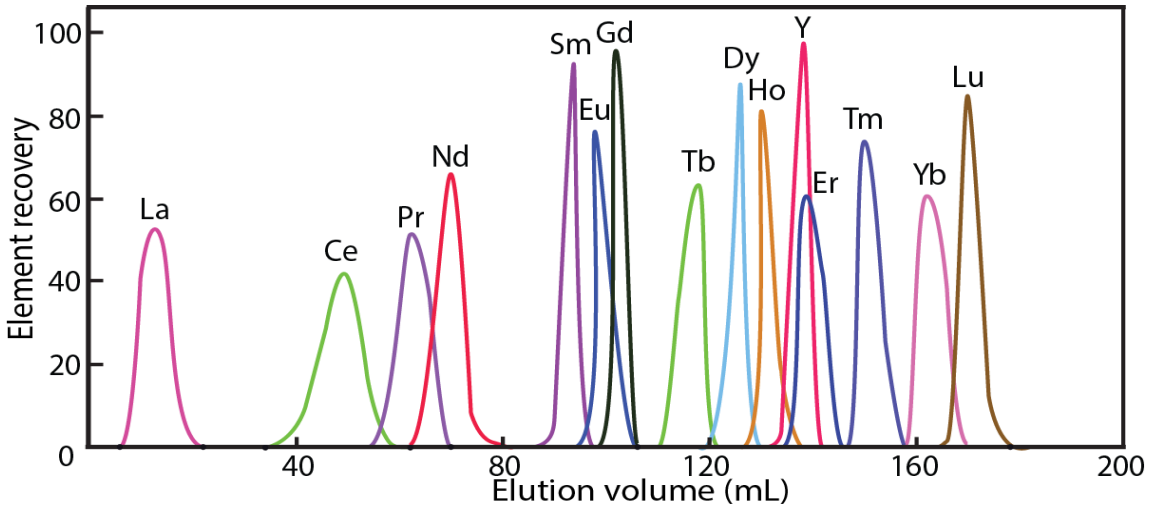

Figure 2: Elution curve of REEs using ChRobot